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Intramolecular Charge Transfer Complexes as
Fluorescence Probes for UV and Visible Light Induced Acrylate
Polymerization

by

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INTRAMOLECULAR CHARGE TRANSFER COMPLEXES AS FLUORESCENCE PROBES FOR UV AND VISIBLE LIGHT INDUCED ACRYLATE POLYMERIZATION

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ABSTRACT

Intramolecular charge transfer complexes (ICTC) of derivatives of 1-diaminonaphthalene-5-sulfonamide (DANSYL AMIDE), such as 1-dimethylamino-naphthalene-5-sulfonyl-n-butylamide (1,5-DASB) and 2-dimethylaminonaphthalene-5-sulfonyl-n-butylamide (2,5-DASB), were used as fluorescence probes for cure monitoring of photocurable polymer systems. This technique is based upon the difference in fluorescence intensity from the parallel and perpendicular conformations of the excited state of the complex, and is based on the dependence of the relative population of each conformation on the microviscosity of the system. As the curing reaction proceeds, the steady state fluorescence emission spectra of the probes were all found to exhibit hypsochromic spectral shifts due to the increase in matrix microviscosity. A linear correlation between the fluorescence intensity ratios ($R=I_{\text{par}}/I_{\text{per}}$) and the extent of polymerization, measured by transmission FTIR spectrometry, was obtained for different types of acrylated polymers, cured with UV or visible (VIS) initiators.

INTRODUCTION

Photocurable polymers are used as coatings for various substrates, such as metals, glass, plastics, wood, floors and paper.¹ Highly crosslinked polymer networks can be rapidly formed via photopolymerization of multifunctional monomers, especially acrylics. The ultimate properties of these polymeric networks depend on various factors, such as monomer structure, forms of

initiation, reaction conditions and the rate and degree of polymerization. Thus, a thorough understanding of the photocuring process is essential to property control and process optimization of the final products.

Several methods have been developed to study the kinetics of photopolymerization. Among them are photo-differential scanning calorimetry (PDSC),²⁻⁵ laser interferometry,⁶ photoacoustic spectroscopy⁷, and UV and FTIR spectroscopy.⁸⁻¹⁰ PDSC is basically like a modified DSC, with a Hg lamp source mounted next to the sample. It has been extensively used to study the kinetics of photopolymerization and the degree of cure can also be measured. However, PDSC is not useful for real time cure monitoring and non-destructive analysis of photopolymers. FTIR is widely used to determine the degree of photopolymerization by monitoring the concentration of residual monomers present in various polymer systems. A real time infra-red (RTIR) technique developed by Decker et al.^{8,9} allows one to monitor the polymerization process continuously and rapidly in real time. Both the rate and degree of polymerization can be measured. However, IR techniques can only be used to analyze thin films (less than 20 μm thick). Besides that, transmission IR techniques cannot be used to monitor the degree of polymerization of coatings on opaque substrates. Also, they are not useful for monitoring polymerization of bulk materials, such as parts made by stereolithography, which is a technique designed to form three dimensional objects by the assembly of a series of photopolymers layers.¹¹

Fluorescence spectroscopy has gained considerable interest due to its high sensitivity, selectivity and non-destructive characteristics. Remote sensing is readily achieved by using fiber-optic cables to transmit optical signals to and from a polymerization system in real time.

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Recently, Neckers et al.¹²⁻¹⁵ reported the successful use of fluorescence probes to monitor the photo-curing process of polyolacrylate monomers. Two types of fluorescence probes were found to be particularly useful. The first is based on "excimer" (i.e. excited dimer) forming molecules, such as pyrene or its derivatives.¹⁶ The ratio of the emission intensities of the monomer and excimer was found to correlate well with the degree of cure. The second is based on intramolecular charge transfer molecules, such as 4-(N,N-dimethyl-amino)benzonitrile (DMABN), and dansyl amide and its derivatives. DMABN exhibits dual fluorescence corresponding to two different singlet excited states called twisted intramolecular charge transfer (TICT) states.¹⁷ The short wavelength (b^*) band is due to a coplanar (parallel) excited state conformation while the long wavelength (a^*) band originates from a perpendicular conformation. The coplanar conformation is more stable in the ground state because of higher delocalization of the π orbitals. Therefore, the coplanar excited state will be directly populated from the ground state. However, the perpendicular excited state is energetically more stable due to the charge separation. This implies that the molecules are first excited to b^* and then "cross" to a^* , making the population of the perpendicular conformation strongly dependent upon the microenvironment of the TICT molecule. In fact, fluorescence spectra of TICT probes were found to be very sensitive to changes in the microviscosity of the medium. In particular, the ratio of the emission intensities at two different emission wavelengths can be correlated linearly with the degree of cure for various polyolacrylate monomer systems.

In this work we present our recent efforts to develop intramolecular charge transfer (ICT) fluorescence probes for various photopolymerizable coatings. The ICT probes studied were 1-dimethylaminonaphthalene-5-sulfonyl-n-butylamide (1,5-DASB), and 2-dimethylaminonaphthalene-5-sulfonyl-n-butylamide (2,5-DASB).

EXPERIMENTAL SECTION

1. Materials

A mixture of multifunctional acrylates was made by mixing polyethylene glycol-400 diacrylate, PEGA-400 (Monomer-Polymer and Dajac Labs. Inc.), trimethylo propane triacrylate, TMPTA (Sart 351, from

the Sartomer Co.), and dipentaerythritol monohydroxy pentaacrylate, DPHPA (Sartomer 399, from the Sartomer Chemical Co.), on a weight percentage ratio of 20:40:40, respectively. A xanthene dye, 5,7-diiodo-3-butoxy-6-fluorone, DIBF, developed in our group,¹⁸ was utilized as VIS initiator at a concentration of about 1×10^{-3} M. An amine co-initiator N-phenyl glycine, NPG (Aldrich) was also used at a concentration of about 5×10^{-2} M. The co-initiator in this case acts as an electron donor to the excited state of the dye, before the generation of free radicals.¹⁸

For commercial photocurable resins, two types of acrylated polymer coating formulations (Formulation I and II, both with UV initiators) were investigated.

As fluorescence probes either 1,5-DASB or 2,5-DASB were used at a concentration of about 5×10^{-4} M in the photopolymerizable resins.

2. Cure Procedure

An Ar⁺ laser (Omnichrome, model 543-200 MGS) was used for visible light initiated polymerization of multifunctional acrylate monomers. To compare samples with different degrees of cure the laser power varied from 30 to 80 mW. To photocure the commercial acrylate coatings a medium pressure Hg-arc lamp was utilized. The degree of polymerization for different samples was varied by changing the exposure time to the UV lamp.

A few drops of the monomer solution being studied were first squeezed between two NaCl plates with a 15.0 μ m thick teflon spacers at the edges to control the final thickness. The laser beam (2.0 mm diameter) was directed to the sample and scanned at a speed of 13.0 mm/sec using computer controlled reflecting mirrors and data files specifically designed for stereolithography purposes.

Steady state fluorescence emission spectra of samples cured for different period of time were obtained via a Spex Fluorolog-2 spectrophotometer. Remote measurement was carried using a bifurcated fiber-optic cable attached to the excitation and emission monochromators, respectively.

Infra-red measurement of the extent of double bond conversion was accomplished using a Mattson Galaxy Series 6020 FT-IR spectrometer with a spectral resolution of 2 cm^{-1} . The extent of C=C conversion (α) was obtained by using the following equation.

$$\alpha = 1 - A_{\text{acry}}(t) \cdot A_{\text{ref}}(0) / A_{\text{acry}}(0) \cdot A_{\text{ref}}(t) \quad (1)$$

where $A_{\text{acry}}(t)$ and $A_{\text{acry}}(0)$ are the absorbances at 810 cm^{-1} due to the acrylate double bond, after curing times t and zero, respectively. $A_{\text{ref}}(t)$ and $A_{\text{ref}}(0)$ are the reference peak absorbances at 2945 cm^{-1} due to the CH groups, after curing times t and zero, respectively. This reference peak was used as an internal standard to calibrate any thickness fluctuation during the curing process.

RESULTS AND DISCUSSION

1. Comparison of Fluorescence Spectra of 1,5-DASB and 2,5-DASB Probes

Both 1,5-DASB and 2,5-DASB are DANSYL amide derivatives. Previous work by Neckers, et al. showed that 2,5-DASB was useful as a fluorescent probe for photopolymerization of polyolacrylates.¹³ Although 1,5-DASB differs just slightly from 2,5-DASB in the position of dimethyl amino group on the naphthalene ring, their fluorescence spectra differ significantly as shown in Figure 1. The excitation peak positions of 1,5-DASB and 2,5-DASB in a dilute THF solution were found to be at 342 nm and 374 nm, respectively. This is consistent with their UV absorption peak positions, as 1,5-DASB absorbs at a shorter wavelength (330 nm) than 2,5-DASB (374 nm). In contrast the fluorescence emission peak position of 1,5-DASB is at much longer wavelength (494 nm) than that of 2,5-DASB (450 nm). Therefore, the Stokes shift of 1,5-DASB (152 nm) is twice as large as 2,5-DASB (76 nm). A larger Stokes shift is a significant advantage for monitoring photopolymerization since spectral blue shifts in the TICT probe fluorescence emission are often observed as the polymerization proceeds due to the increase in matrix viscosity. The intrinsic fluorescence from the photopolymer (if any) would have less interference to the probe fluorescence with a large Stokes shift value.

2. 2,5-DASB as a Fluorescence Probe for the Degree of Photopolymerization of Multifunctional Acrylate Monomers Using Visible Photoinitiators and Visible Light Emitting Curing Sources.

Table 1 presents results corresponding to the photopolymerization of the mixture of multifunctional acrylate monomers using DIBF and NPG as the initiator

system and an Ar⁺ laser as the irradiation source. The data displayed are the percentages of C=C double bond converted to single bonds by the photopolymerization process, as well as the laser power used for the different samples, and the ratios, R , between the fluorescence intensities at 430 and 500 nm, respectively, corresponding to the emissions from the two conformations of excited state of 2,5-DASB.

Table 1. Results of IR and fluorescence analyses of the degree of polymerization of a multifunctional acrylate monomer solution using 2,5-DASB as a probe. (Initiator = DIBF; Coinitiator = NPG; Irradiation source = Ar⁺ laser).

PI (mW)	% C=C	R (I ₄₃₀ /I ₅₀₀)
30	16.7	1.20
50	22.7	1.26
80	36.2	1.40

When the R values were plotted against the extent of C=C conversion (Figure 2) a very good linear correlation was obtained ($r=0.9999$) with the ordinate intercept (0.0 % C=C) corresponding to the ratio of the fluorescence intensities emitted by the excited states of the probe in solution, before the photopolymerization process. This first test clearly indicated that the technique and probe were well suited to be used in these highly crosslinked photopolymer systems.

3. 1,5-DASB as a Fluorescence Probe of the Degree of Photopolymerization.

(i). Photocurable resins with UV initiators

To investigate the applicability of 1,5-DASB as a fluorescence probe for photo-polymerization, we doped 1,5-DASB at a small concentration into various commercial acrylate coating resins. The probe fluorescence emission spectra in the photopolymer systems studied were monitored as a function of irradiation time. As the curing reaction proceeds, fluorescence emission peak position exhibits blue shifts due to increases in the medium viscosity which makes it more difficult to form the long wavelength charge transfer excited state. Figure 3 compares the fluorescence emission spectra of 1,5-DASB probe in a

commercial photocurable acrylate (Formulation I) before and after a full curing (30 seconds under a medium pressure Hg lamp). A total spectral blue shift of about 20 nm was obtained. Similar to what described previously,¹⁵ we monitored changes in fluorescence intensity ratios as a function of irradiation time as illustrated in Figure 4. It can be seen that the general trends in the three cases ($R = I_{470}/I_{560}$, I_{470}/I_{550} and I_{470}/I_{540}) are about the same.

Linear correlations between the extent of double bond conversion of Formulation I vs. the fluorescence intensity ratio of the fluorescence probe were obtained for all the three cases examined ($R = I_{470}/I_{560}$, I_{470}/I_{550} and I_{470}/I_{540}), as shown in Figure 5. However, the intensity ratio of I_{470}/I_{560} was found to give the best linear correlation. Therefore, we chose to use I_{470}/I_{560} as the probe parameter to monitor the photopolymerization of multifunctional acrylates.

Figure 6 compares the changes in the extent of double bond conversion as a function of irradiation time for the two formulations studied. We can see that the initial cure rate of Formulation I is significantly slower than that of Formulation II. An induction time of about two seconds was observed for Formulation I while that of Formulation II was less than one tenth of a second. However, the overall extent of cure of the Formulation I (~95 %) was much higher than that of Formulation II (~60 %). This is probably due to the rapid increase in crosslinking density due to a fast cure rate in Formulation II that makes the diffusion of radicals difficult, resulting in a lower extent of polymerization.

Figure 7 gives the linear correlation plots of I_{470}/I_{560} vs. the extent of double bond conversion for the two commercial formulations, showing similar slopes. The mathematical expressions given in Equations 2 and 3 can be used to correlate the fluorescence intensity ratio (I_{470}/I_{560}) with the extent of C=C conversion (α) for Formulations I and II, respectively.

$$R = 1.6284 + 2.3197\alpha \quad (2)$$

$$R = 1.3804 + 2.6314\alpha \quad (3)$$

(ii). Multifunctional acrylates with visible initiators

Visible initiators such as fluorone derivatives exhibit fluorescence emission in photopolymers with low

degree of polymerization and an incomplete photo-bleaching of the photo-initiators. It is interesting to know the effects of visible initiators on the fluorescence spectra of the 1,5-DASB probe. Thus we investigated the applicability of the new fluorescence probe to monitor the photo-curing reaction of multifunctional acrylates initiated via the visible dye initiators developed in our laboratories.¹⁸ The monomer solution contains TMPTA/DHPA (1:1 molar), polyethylene glycol, DIBF (initiator) and NPG (coinitiator). The fluorescence emission intensity ratio (I_{470}/I_{560}) of 1,5-DASB probe was found to increase from 1.1 (0% conversion) to about 2.2 (32% conversion) after 60 seconds of irradiation under a medium pressure Hg lamp. A linear correlation plot of the probe fluorescence intensity ratio vs. the extent of C=C conversion was obtained as shown in Figure 8. The linear relationship between R (I_{470}/I_{560}) and the extent of conversion (α) is given in Equation 4.

$$R = 1.1167 + 3.3908\alpha \quad (4)$$

SUMMARY

Intramolecular charge transfer complexes (ICTC) fluorescence probes such as 1-dimethylamino-naphthalene-5-sulfonyl-n-butylamide (1,5-DASB) and 2-dimethylaminonaphthalene-5-sulfonyl-n-butyl-amide (2,5-DASB) are useful for cure monitoring of photocurable polymer systems with UV or visible initiators. As the curing proceeds, the steady state fluorescence emission spectra of the probes were all found to exhibit hypsochromic spectral shifts due to the increases in matrix microviscosity. Linear correlations between the fluorescence intensity ratios and the extent of polymerization were obtained. With a fiber-optic fluorimeter, this fluorescence cure sensing technique based on ITCT fluorescence probes can be readily applied to photopolymerized films, coatings and bulk materials.

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18. Neckers, D. C.; Tanabe, T., unpublished.
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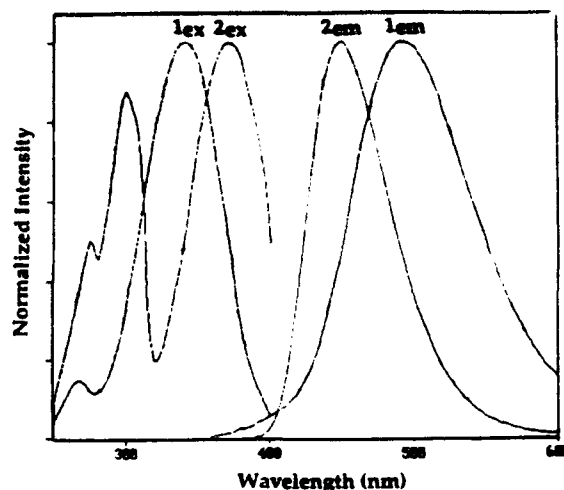


Fig. 1. Fluorescence excitation (EX) and emission (EM) spectra of 1,5-DASB (1) and 2,5-DASB (2), respectively, in THF.

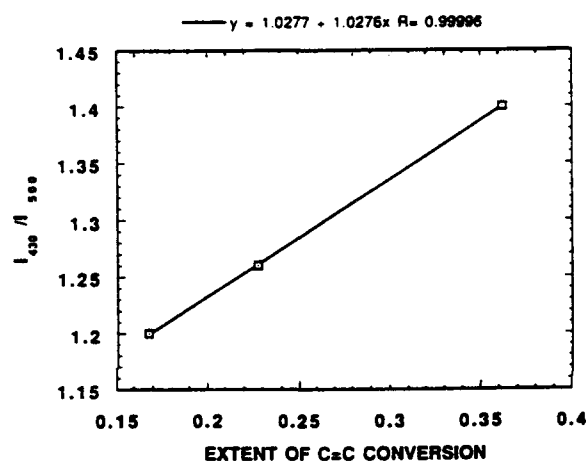


Fig. 2. Correlation plot of the fluorescence intensity ratio (I_{430}/I_{500}) vs. the extent of C=C conversion of a multifunctional acrylate monomer system with a visible initiator (DIBF) and cured by an Ar^+ laser.

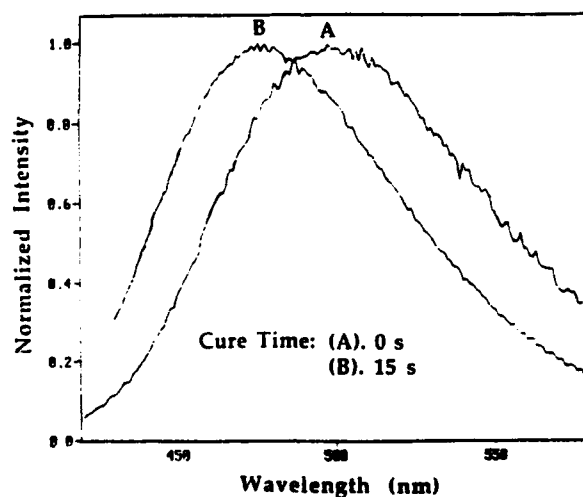


Fig. 3. Fluorescence emission spectra of 1,5-DASB in a commercial photocurable resin (Formulation I) as a function of irradiation time using a medium pressure Hg lamp. (Excitation at 380 nm).

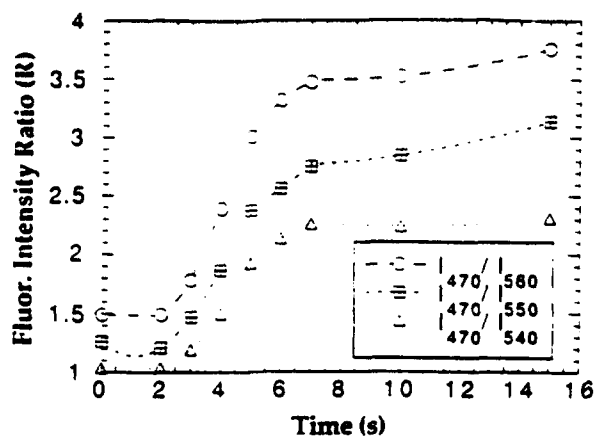


Fig. 4. Changes in fluorescence intensity ratios of 1,5-DASB in a commercial photocurable resin (Formulation I) as a function of irradiation time using a medium pressure Hg lamp. (Excitation at 380 nm).

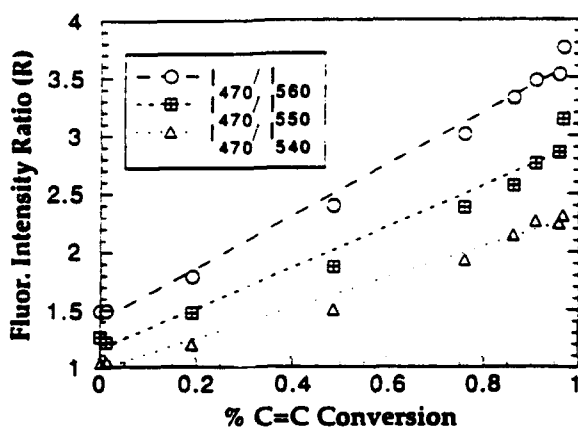


Fig. 5. Linear correlation plot of the fluorescence intensity ratios ($R = I_{470}/I_{560}$, I_{470}/I_{550} and I_{470}/I_{540}) of 1,5-DASB vs. the extent of C=C conversion in Formulation I.

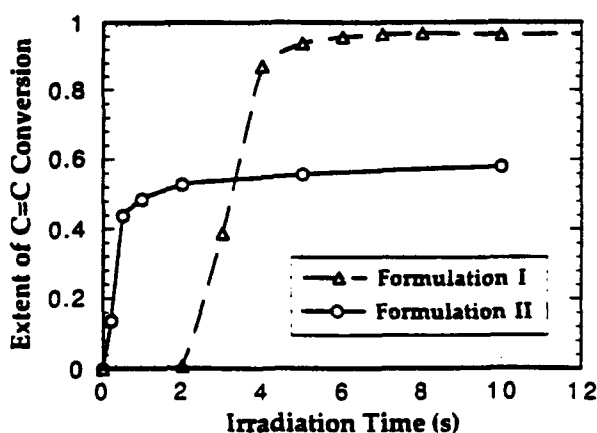


Fig. 6. Changes in the C=C conversion of two commercial photocurable resins (Formulations I and II) as a function of irradiation time using a medium pressure Hg lamp.

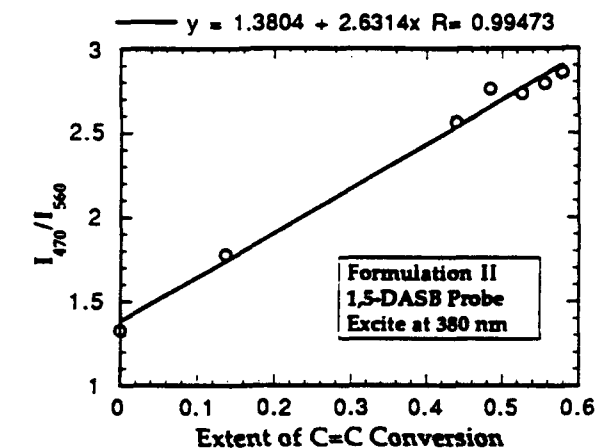
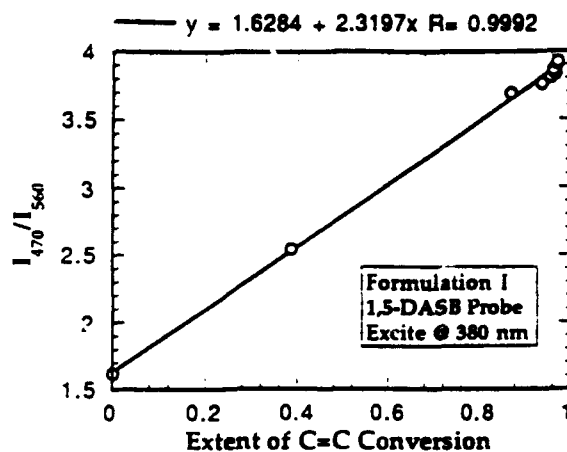


Fig. 7. Linear correlation plot of the fluorescence intensity ratio ($R = I_{470}/I_{560}$) of 1,5-DASB vs. the extent of C=C conversion for two commercial photocurable resins.

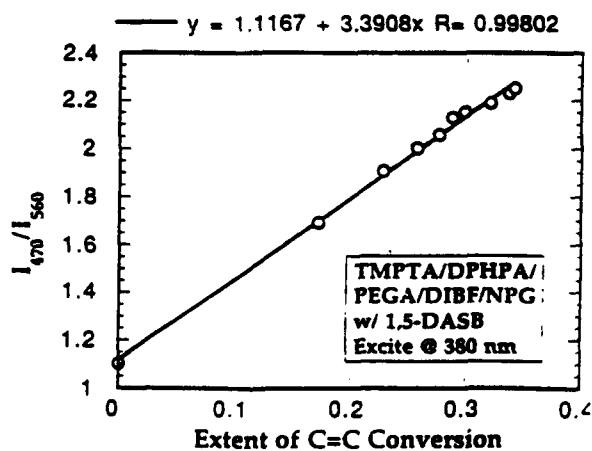


Fig. 8. Linear correlation plot of the fluorescence intensity ratio ($R = I_{470}/I_{560}$) of 1,5-DASB vs. the extent of C=C conversion of a multifunctional acrylate system with a visible initiator (DIBF) and an amine coinitiator (NPG).